

Practitioner's Docket No. U 013762-9

10/009939

Optional Customer No. Bar Code



00140

PATENT TRADEMARK OFFICE

CHAPTER II

TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)

(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)

| | | |
|--|---------------------------|-----------------------|
| PCT/FR00/01852 | 30 JUNE 2000 | 7 JULY 1999 |
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
| METHOD AND DEVICE FOR STEAM CRACKING OF HYDROCARBONS | | |
| TITLE OF INVENTION | | |
| SERGE BELLET, JEAN PINON | | |
| APPLICANT(S) | | |

Box PCT
Assistant Commissioner for Patents
Washington D.C. 20231
ATTENTION: EO/US

NOTE: The completion of those filing requirements that can be made at a time later than 30 months from the priority date

CERTIFICATION UNDER 37 C.F.R. 1.10*
(Express Mail label number is *mandatory*.)
(Express Mail certification is *optional*.)

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on this date December 11, 2001, in an envelope as "Express Mail Post Office to Addressee," Mailing Label Number EV011019612US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

JENNIFER RASHKIN

(type or print name of person mailing paper)

Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" *must* have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. 1.10(b).
"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will *not* be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

10009939-028220-6660007

results from the Commissioner exercising his judgment under the authority granted under 35 USC 371(d). The filing receipt will show the actual date of receipt of the last item completing the entry into the national phase. See 37 C.F.R. §1.491 which states: "An international application enters the national state when the applicant has filed the documents and fees required by 35 USC 371(c) within the periods set forth in § 1.494 and § 1.495."

WARNING: Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. §1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing - See 37 C.F.R. §1.8.

NOTE: Documents and fees must be clearly identified as a submission to enter the national state under 35 USC 371 otherwise the submission will be considered as being made under 35 USC 111. 37 C.F.R. § 1.494(f).

1. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. 371:

- a. ☒ This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).
- b. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

1009939-02202

2.Fees

| CLAIMS FEE | (1) FOR | (2) NUMBER FILED | (3) NUMBER EXTRA | (4) RATE | (5) CALCULATIONS |
|--------------|---|------------------|------------------|--------------|------------------|
| []* | TOTAL CLAIMS | 21- 20 = | 1 | x \$ 18.00 = | \$18.00 |
| | INDEPENDENT CLAIMS | 2- 3 = | | x \$ 84.00 = | |
| | MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$280.00 | | | | |
| BASIC FEE** | [] U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an International preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: [] and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(2) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 CFR 1.492(a)(4)) \$100.00 [] and the above requirements are not met (37 CFR 1.492(a)(1)) \$710.00 [X] U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: [] has been paid (37 CFR 1.492(a)(2)) \$740.00 [] has not been paid (37 CFR 1.492(a)(3)) \$1,040.00 [X] where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 CFR 1.492(a)(5)) \$890.00 | | | | |
| | Total of above Calculations | | | | =\$908.00 |
| SMALL ENTITY | Reduction by ½ for filing by small entity, if applicable. Statement may also be filed. (note 37 CFR 1.9, 1.27, 1.28) | | | | - |
| | Subtotal | | | | \$908.00 |
| | Total National Fee | | | | \$908.00 |
| | Fee for recording the enclosed assignment document \$40.00 (37 CFR 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET". | | | | |
| TOTAL | Total Fees enclosed | | | | \$908.00 |

*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ☒ A check in the amount of \$908.00 to cover the above fees is enclosed.
 ii. ☐ Please charge Account No. _____ in the amount of \$ _____.
 A duplicate copy of this sheet is enclosed.

****WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: * * * (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

WARNING: If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☒ A copy of the International application as filed (35 U.S.C. 371(c)(2)):

NOTE: Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☐ is transmitted herewith.
 b. ☐ is not required, as the application was filed with the United States Receiving Office.
 c. ☒ has been transmitted
 i. ☒ by the International Bureau.
 Date of mailing of the application (from form PCT/IB/308):
January 18, 2001.
 ii. ☐ by applicant on _____
 Date

4. ☒ A translation of the International application into the English language (35 U.S.C. 371(c)(2)):
 a. ☒ is transmitted herewith.
 b. ☐ is not required as the application was filed in English.
 c. ☐ was previously transmitted by applicant on _____
 Date
 d. ☐ will follow.

- NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.*

- (Transmittal Letter to the United States Elected Office (EO/US)—page 5 of 8) 13-18

10/009939

JPPT Res: 727/10 11 DEC 2007

10. ☒ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)) complying with 35 U.S.C. 115
- a. ☐ was previously submitted by applicant on _____.
Date
- b. ☐ is submitted herewith, and such oath or declaration
- i. ☐ is attached to the application.
- ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. 1.70.
- c. ☒ will follow.

Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):
- a. ☒ is transmitted herewith.
- b. ☐ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): _____.
- c. ☐ is not required, as the application was searched by the United States International Searching Authority.
- d. ☐ will be transmitted promptly upon request.
- e. ☐ has been submitted by applicant on _____.
Date
12. ☒ An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98:
- a. ☒ is transmitted herewith.
Also transmitted herewith is/are:
☒ Form PTO-1449 (PTO/SB/08A and 08B).
☒ Copies of citations listed.
- b. ☐ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. 371(c).
- c. ☐ was previously submitted by applicant on _____.
Date

13. ☐ An assignment document is transmitted herewith for recording.

A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

14. ☒ Additional documents:
- a. ☒ Copy of request (PCT/RO/101)
 - b. ☒ International Publication No. WO 01/04236 A1
 - i. ☐ Specification, claims and drawing
 - ii. ☒ Front page including drawing
 - c. ☒ Preliminary amendment (37 C.F.R. § 1.121)
 - d. ☒ Other

FORM PCT/IPEA/416, FORM PCT/IB/308

15. ☒ The above checked items are being transmitted
- a. ☒ before 30 months from any claimed priority date.
 - b. ☐ after 30 months.

16. ☐ Certain requirements under 35 U.S.C. 371 were previously submitted by the applicant on _____, namely:

AUTHORIZATION TO CHARGE ADDITIONAL FEES

WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges if extra claims are authorized.*

NOTE: *"A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).*

NOTE: *"Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).*

- ☒ The Commissioner is hereby authorized to charge the following additional fees that may be required by this paper and during the entire pendency of this application to Account No. 12-0425.

- ☒ 37 C.F.R. 1.492(a)(1), (2), (3), and (4) (filing fees)

WARNING: *Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box.*

- ☐ 37 C.F.R. 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

- ☒ 37 C.F.R. 1.17 (application processing fees)
☒ 37 C.F.R. 1.17(a)(1)-(5)(extension fees pursuant to § 1.136(a).
☒ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

- [] 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).


 SIGNATURE OF PRACTITIONER

WILLIAM R. EVANS

(type or print name of practitioner)

Reg. No.: 25,858

Tel. No.: (212) 708-1930

P.O. Address

Customer No.: 00140

c/o Ladas & Parry
 26 West 61st Street
 New York, N.Y. 10023

10/009939

JC05 Rec'd PCT/PTC 1 1 DEC 2001

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: SERGE BELLET, et al.
International Application No.: PCT/FR 00/01852
International Filing Date: June 30, 2000 Priority Date Claimed: July 7, 1999
For: Method and device for stream cracking of hydrocarbons

Attorney Docket No.: U 013762-9

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

Please amend the above application as follows.

IN THE CLAIMS

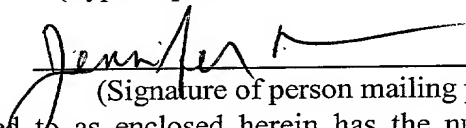
4. (Amended) A method according to claim 1, characterized in that the mechanical work is produced by a heat engine, a gas engine, or preferably a gas turbine.
5. (Amended) A method according to claim 1, characterized in that the cogeneration produces heat energy in the form of hot combustion gases at a temperature lying in the range 400°C to 570°C, and preferably in the range 470°C to 550°C.

CERTIFICATE UNDER 37 CFR 1.10

I hereby certify that this paper is being deposited with the United States Postal Service on this date December 11, 2001 in an envelope as "EXPRESS MAIL POST OFFICE TO ADDRESSEE" Mailing Label Number EV011019612US addressed to the: Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

JENNIFER RASHKIN

(Type or print name of person mailing paper)


(Signature of person mailing paper)

NOTE: Each paper or fee referred to as enclosed herein has the number of the "EXPRESS MAIL" mailing label place thereon prior to mailing 37 CFR 1.16(b).

10009939.022802

6. (Amended) A method according to claim 1, characterized in that the cogeneration produces the heat energy in the form of hot combustion gases, with a fraction of the oxygen thereof being used as oxidizer for performing post-combustion and increasing the heat energy used for preheating the mixture to be cracked.

9. (Amended) A method according to claim 1, characterized in that electrical heating is performed by induction heating.

11. (Amended) A method according to claim 1, characterized in that the electrical heating is performed by the Joule effect.

13. (Amended) A method according to claim 1, characterized in that ultrasound waves are applied to the mixture of hydrocarbons and steam during cracking.

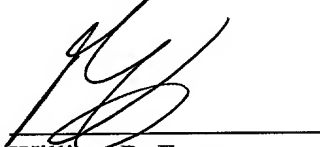
19. (Amended) Apparatus according to claim 15, characterized in that it comprises at least one post-combustion chamber (10) placed on at least one of the lines (9) for evacuating combustion gases from the gas turbine (1) and fed by a fuel feed line.

20. (Amended) Apparatus according to claim 15, characterized in that the zone (17) for separating and purifying the cracked hydrocarbons comprises at least one drawing-off line (19) for drawing off at least one cracked hydrocarbon, and in that said drawing-off line (19) has at least one recovery line (5) running therefrom for recovering at least one cracked hydrocarbon and connected to at least one of the lines (3) for feeding fuel to the gas turbine (1).

REMARKS

The above amendatory action is taken solely for the purpose of avoiding claim fees that would otherwise accrue due to the presence of multiple dependent claims.

Respectfully submitted

A handwritten signature in black ink, appearing to be 'W. Evans', written over a horizontal line.

William R. Evans
c/o Ladas & Parry
26 West 61st Street
New York, New York 10023
Reg. No.: 25,858 (212) 708-1930

10009939 022803

MARKED-UP COPY

4. (Amended) A method according to [any one of claims] claim 1 [to 3], characterized in that the mechanical work is produced by a heat engine, a gas engine, or preferably a gas turbine.
5. (Amended) A method according to [any one of claims] claim 1 [to 4], characterized in that the cogeneration produces heat energy in the form of hot combustion gases at a temperature lying in the range 400°C to 570°C, and preferably in the range 470°C to 550°C.
6. (Amended) A method according to [any one of claims] claim 1 [to 5], characterized in that the cogeneration produces the heat energy in the form of hot combustion gases, with a fraction of the oxygen thereof being used as oxidizer for performing post-combustion and increasing the heat energy used for preheating the mixture to be cracked.
9. (Amended) A method according to [any one of claims] claim 1 [to 8], characterized in that electrical heating is performed by induction heating.
11. (Amended) A method according to [any one of claims] claim 1 [to 8], characterized in that the electrical heating is performed by the Joule effect.
13. (Amended) A method according to [any one of claims] claim 1 [to 12], characterized in that ultrasound waves are applied to the mixture of hydrocarbons and steam during cracking.
19. (Amended) Apparatus according to [any one of claims] claim 15 [to 18], characterized in that it comprises at least one post-combustion chamber (10) placed on at least one of the lines (9) for evacuating combustion gases from the gas turbine (1) and fed by a fuel feed line.
20. (Amended) Apparatus according to [any one of claims] claim 15 [to 19], characterized in that the zone (17) for separating and purifying the cracked hydrocarbons comprises at least one drawing-off line (19) for drawing off at least one cracked hydrocarbon, and in that said drawing-off line (19) has at least one recovery line (5) running therefrom for recovering at least one cracked hydrocarbon and connected to at least one of the lines (3) for feeding fuel to the gas turbine (1).

20090929 09:00

10/009939

JC05 Rec'd PGT/PTO 1 1 DEC 2001

1

A METHOD AND APPARATUS FOR STEAM CRACKING HYDROCARBONS

The present invention relates to a method of steam cracking hydrocarbons in order to produce olefins, in particular.

5 A known steam cracking method consists in causing a mixture of hydrocarbons and steam to pass along at least one cracking tube such as a coil placed in a furnace. On being raised to high temperature, e.g. in the range 700°C to 900°C, the hydrocarbons are cracked so as to provide
10 olefins in particular and possibly also diolefins and light alkanes such as methane. It will readily be understood that it is not possible to raise the hydrocarbons for cracking instantly to the desired reaction temperature, and that this temperature varies
15 progressively along the cracking tube in application of a profile that is more or less steep, in particular when passing through preheating zones.

As a general rule, a steam cracking furnace uses radiant heat delivered by burners such as conventional
20 gas or oil burners as its source of heat. The burners are often placed on the floor and/or the walls of the furnace and they define a high temperature zone in the furnace, also referred to as the "radiation" zone of the furnace. Immediately above said zone, there is a
25 convection zone through which the hot combustion gases escape from the radiation zone, which convection zone is generally used for preheating the mixture of hydrocarbons to be cracked, also known as the "feedstock" to be cracked. Thus, the mixture is usually preheated to about
30 500°C in the convection zone of a furnace, after which it enters the radiation zone of the furnace where it reaches the reaction temperature, in particular a temperature in the range 700°C to 900°C.

Such a method thus consists in performing an entire
35 heat treatment program from the preheating stage to the cracking stage proper within a single heating furnace, using the radiant heat from the burners as the source of

heat. The furnace must be capable of withstanding the highest temperatures involved in the method, and it must also be a piece of equipment that is large in size, with all of the manifest drawbacks associated with size.

5 The method of steam cracking also requires accurate control over heating in the reaction zone, i.e. the high temperature zone. With furnaces that use the radiant heat delivered by burners as the source of heat, and insofar as all of the inside space of the furnace is
10 heated by said radiant heat, temperature can only be controlled indirectly, and thus inaccurately.

US patent No. US 4 912 282 describes a method and apparatus for steam cracking hydrocarbons to produce olefins such as ethylene. The apparatus comprises a
15 cracking furnace that is heated by burning fuel using an oxidizer comprising a mixture of air and exhaust gas from a gas turbine that forms part of a cogenerator system. The gas turbine is coupled to an electricity generator which feeds electricity to compressors and pumps. The
20 combustion air as preheated in that method enables the combustion temperature to be increased and thus enables the efficiency of the radiation zone (high temperature zone) of the cracking furnace to be increased, and consequently enables fuel consumption to be reduced.
25 Nevertheless, temperature control in the radiation zone of the cracking furnace remains inaccurate, and the size of the furnace is very large. Furthermore, a high level of harm continues to be done to the environment by nitrogen oxide being rejected to the atmosphere together
30 with the combustion gases from the cracking furnace.

European patent application No. EP 0 806 467 describes a method of pyrolyzing hydrocarbons which is performed together with a continuous decoking method specifically for the purpose of reducing or eliminating
35 the losses of time usually associated with stops for decoking. The pyrolysis method includes a prior step of steam cracking in a steam cracking furnace followed by

10009939 022802

the pyrolysis step proper which is performed in a pyrolysis reactor at very high temperature and which is intended to produce acetylene hydrocarbons such as acetylene. It is specified that the steam cracking furnace is normally heated by conventional gas burners, e.g. of the radiant burner type, and that the pyrolysis reactor can be heated either by electrical resistances or by jackets containing gas burners. There is no description nor suggestion of the electrical resistances being powered electrically by a cogenerator system. Furthermore, it is mentioned that electrical heating is not at all to be recommended for such a reactor because of high investment and running costs.

Japanese patent application JP 09 235 564 proposes a method of thermally cracking hydrocarbons to produce ethylene. In that method, the feedstock is preheated by means of the combustion heat from a preheating furnace provided with conventional burners, and is then subjected to thermal cracking in a high temperature zone by means of induction heating. Nevertheless, the electricity required for the induction heating does not come from a cogenerator system. Furthermore, the preheating furnace is provided with conventional burners with all of the above-mentioned drawbacks for that type of heating associated in particular with environmental problems such as rejecting nitrogen oxides to the atmosphere together with the combustion gases of such a furnace.

The present invention relates to a method of steam cracking hydrocarbons that makes it possible to avoid or reduce very significantly the drawbacks mentioned above. In particular, the invention provides a method of steam cracking hydrocarbons, which method consists in heating a mixture of hydrocarbons and steam to a desired temperature that is high enough to crack the hydrocarbons and transform them into olefins, the method being characterized in that the source of energy needed for heating the mixture is supplied essentially by

10009939.022803

cogeneration using combustion of a fuel to produce simultaneously both heat energy and mechanical work which is transformed into electricity by an alternator or an electricity generator, and in that the mixture is initially subjected to preheating using the heat energy supplied by the cogeneration, and is subsequently heated to the desired cracking temperature by means of electrical heating using the electricity supplied by the cogeneration.

Figure 1 is a diagram of apparatus for implementing the method of the present invention.

The steam cracking method of the present invention is particularly advantageous when the cogeneration uses fuel selected from at least one of the cracked hydrocarbons (i.e. as obtained by the cracking), in particular one or more gaseous alkanes e.g. in the range C_1 to C_4 , and preferably methane. Under such circumstances, the fuel is preferably a gaseous hydrocarbon fuel.

Using a preferably gaseous fuel for combustion purposes enables cogeneration to produce simultaneously both heat and mechanical work. The mechanical work as produced by a heat engine or a gas engine, for example, or preferably by a gas turbine, is generally used to drive at least one alternator that produces electricity. By recovering the heat energy that is normally lost when producing mechanical work, cogeneration thus provides both heat and mechanical work which can be reused in appropriate and advantageous manner.

The cogeneration implemented in the present invention advantageously gives self-contained control and management over the production of electricity adapted to the specific requirements of the electrical heating, e.g. by selecting the power and/or the frequency of the electricity to be suitable for achieving the desired high temperatures for cracking. Furthermore, cogeneration, which preferably uses a gaseous fuel such as natural gas

10009939-022802

or preferably one or more of the hydrocarbons produced by the cracking, e.g. alkanes in the range C_1 to C_4 and in particular methane, has the advantage of providing not only significant energy savings, but also a solution to concerns related to combating atmospherical pollution, in particular by minimizing the amount of nitrogen oxides that are rejected into the atmosphere together with the combustion gases.

The method of the present invention presents enormous potential associated with accurate control over the temperature profile in the electrical heating zone where the hydrocarbons are cracked. It provides greater flexibility in selection of the temperature profile, thus making it possible to optimize the cracking of hydrocarbons.

The method of the present invention advantageously presents implementation that is much simpler than that required for previously known steam cracking methods. It also has the enormous advantage of being economically viable.

Cogeneration in particular by means of a gas turbine generally comprises: a) compressing fresh air or oxidizer (containing oxygen) to an absolute pressure of 1.5 megapascals (MPa) to 2.5 MPa, for example, depending on the desired electrical power; then b) introducing the air or oxidizer as compressed in this way and as mixed with the preferably gaseous fuel into a combustion chamber to perform combustion; then c) after combustion, expanding the hot combustion gases in a turbine that is generally coupled to at least one generator or alternator producing electricity; and d) recovering the hot combustion gases as a source of heat. A portion of the mechanical work that is produced can be used for the initial compression of air or oxidizer, e.g. by driving an air turbocompressor.

In the method of the present invention, the temperature of the hot combustion gases delivered by the

5

10

35

as a countercurrent to said exhaust gases, for example, by passing in succession through one or more preheating and superheating zones. It is also possible, optionally, to exchange the heat of these exhaust gases simultaneously with water or steam in one or more boilers so as to produce the hot water or the steam at low or medium pressure (e.g. 0.1 MPa to 12 MPa) and increase the energy efficiency of the method. The steam produced in this way can be used in situ as a source of energy in the steam cracking method and in particular during the steps of separating, fractioning, and purifying the olefins and light alkanes that are produced.

During post-combustion, part of the oxygen contained in the hot gases from the cogeneration is consumed so that the oxygen content of the post-combustion exhaust gas can lie in the range 1% to 10% and preferably in the range 1% to 5%, by volume. The temperature of the post-combustion exhaust gas after heat exchange with the mixture for cracking is substantially decreased and can lie in the range 120°C to 300°C, and preferably in the range 150°C to 250°C.

The mixture of hydrocarbons and of steam can thus be preheated by passing through one or more preheating and possibly superheating zones, essentially by convection in heat exchangers exchanging heat with the combustion of gas from the cogeneration or preferably the exhaust gas from post-combustion as described above. The temperature of the mixture after preheating can reach 400°C to 600°C, and preferably lies in the range 450°C to 550°C.

By way of example, it is possible to use a cogenerator system constituted by a "Frame 9"® type gas turbine from General Electric capable of delivering 120 megawatts (MW) of electrical power. The heat power which can be produced downstream from that system is 130 MW, and it can be raised up to 150 MW if post-combustion of the kind described above is implemented. Under such circumstances, the cogenerator system has the

energy capacity to run steam cracking furnaces with a total capacity of 300,000 (metric) tonnes per annum of ethylene.

5 The preheated mixture is then heated to the cracking temperature by means of electrical heating powered with the electricity produced by the cogeneration. One of the advantages of the present invention is to be able to adapt at will the amount of electricity provided on site by the cogeneration, and in particular to adapt the
10 electrical power and/or frequency to the specific requirements of the electrical heating, and thus reach the desired cracking temperature throughout the cracking tube(s), in particular in application of a determined temperature-increase profile up to the desired maximum
15 cracking temperature.

The electrical heating techniques used for reaching the desired cracking temperature can be induction heating or Joule effect heating, e.g. by means of a resistance element tube.

20 With induction heating, the mixture for cracking can be heated in a heating furnace by induction. The furnace can comprise a plurality of induction heater tubes that are connected together in parallel. The preheated mixture of hydrocarbons and steam flows inside the tubes
25 where it is subjected to thermal cracking suitable for forming olefins, and this is done in said high temperature range obtained by means of the induction furnace. The induction heating tubes can be inside an enclosure which is closed and leaktight. Each induction
30 heating tube can comprise a tube (or "cracking" tube) carrying a flow of the preheated mixture of hydrocarbons and steam, together with an inductor coil wound around the tube. Lagging can be placed between the tube and the coil and further lagging can be placed over the coil as
35 an outer covering. The coil can be constituted by a winding of copper wire. A generator or alternator, e.g. operating at high frequency, can be connected to the ends

10009939-102200

of the coil so as to power the coil electrically, e.g. at high frequency. The generator or alternator can be part of the cogeneration and can deliver exactly the amount of electricity required for induction heating. The generator or the alternator can also be connected to a frequency and power adapter delivering electricity suitable for induction heating of the tube(s) in which the steam cracking reaction is performed.

Induction heating is preferably performed at high frequency (HF), in particular at frequencies lying in the range 3 megahertz (MHz) to 30 MHz, e.g. frequencies of 13 MHz and 27 MHz. Induction heating is not limited to HF induction: it is also possible to use intermediate frequencies in the range 1 kilohertz (kHz) to 3 MHz, e.g. 2000 hertz (Hz), or a commercial induction frequency in the range 50 Hz to 100 Hz, e.g. 50 Hz or 60 Hz.

By way of example, it is possible to use induction heating and in particular the heating apparatus and HF heating tubes described in Japanese patent application JP 09 235 564.

When Joule effect heating is used, the mixture for cracking can be heated in one or more resistance element tubes, by applying electrical voltage between the ends of said tubes carrying the mixture. The heater device based on resistance element tubes comprises one or more tubes in which the mixture of hydrocarbons and steam flows, said tubes being made out of a conductive material, e.g. stainless steel, and said tubes being connected to a voltage generator. The tubes thus act to perform the following functions simultaneously: transport; electrical resistance elements; and heat exchanger surface. The electrical voltage applied to the resistance element tube(s) can be generated by a low voltage or very low voltage transformer powered by the generator or alternator forming part of the cogenerator system.

Heating by means of a resistance element tube is preferably implemented by using electricity at a voltage

1000933 02280

of less than 50 volts (V), thus ensuring safety for personnel. A power modulator can advantageously be used to control the temperature of the mixture of hydrocarbons and steam.

5 It is also possible to use a tube that vibrates when carrying electricity. Under such circumstances, the resistance element tube is subjected to transverse vibration, in particular at a frequency close to a resonant frequency of the tube. This has the advantage
10 of reducing coke deposition on the inside wall of the resistance element tube, as described in European patent No. EP 0 519 050.

By way of example, it is possible to use resistance element tubes of the kinds sold by the following French
15 companies: Etirex, Parmilleux, and Vulcanic.

It is also possible to use a resistance element tube associated with apparatus that enables induction heating to be performed simultaneously.

In a preferred embodiment of the present invention,
20 ultrasound waves can be applied to the mixture of hydrocarbons and steam during cracking, as described in US patent No. US 3 819 740. It is possible to use an ultrasound wave generator powered using the electricity provided by the cogeneration. The frequency of the
25 ultrasound waves supplied to the mixture for cracking in the electrical heater apparatus can lie in the range 1 kHz to 800 kHz, e.g. being 10 kHz or 20 kHz. It has been found that applying ultrasound waves during steam cracking of the hydrocarbon mixture serves to avoid or at
30 least reduce internal coking of the cracking tubes and also serves to improve the selectivity of the steam cracking reaction.

The mixture of hydrocarbons and steam is subjected to a cracking temperature which can generally begin at an
35 inlet temperature to the electrical heater apparatus lying in the range 400°C to 700°C, preferably in the range 450°C to 660°C, and which can generally end at a

1000939.022802

maximum or outlet temperature from said apparatus lying in the range 700°C to 900°C, and preferably in the range 760°C to 850°C. Between the inlet and the outlet of the electrical heater apparatus, the cracking temperature can increase along the cracking tubes in application of a profile that is continuous or discontinuous as described in European patents Nos. EP 0 252 355 and EP 0 252 356. The mean transit time of the mixture of hydrocarbons and steam between the inlet and the outlet of the electrical heating apparatus can lie in the range 300 milliseconds (ms) to 1800 ms. The reaction volume can be constant or varying all along the cracking tubes between the inlet and the outlet of the electrical heater apparatus, as described in the two above-cited European patents.

The present invention also provides hydrocarbon steam cracking apparatus comprising:

i) a cogenerator system comprising a gas turbine (1) connected to a line (2) for supplying it with air or oxidizer, to a line (3) for feeding it with fuel, and to at least one exhaust line (9) for exhausting hot combustion gases from the gas turbine (1), the turbine itself being coupled to at least one alternator or electricity generator (4) connected to at least one electrical line (8);

ii) at least one preheating chamber (14) for preheating a mixture of hydrocarbons and steam, the chamber being connected to at least one of the lines (9) for evacuating hot combustion gases and having at least one line (12) passing therethrough for transporting said mixture and enabling heat to be exchanged therewith;

iii) at least one electrical heater apparatus for heating at least one cracking tube (6) connected to at least one of the transport and heat exchange lines (12) leaving the chamber (14), and at least one drawing-off line (16) for drawing off cracked hydrocarbons, said electrical heater apparatus being connected to at least one of the electrical lines (8); and

iv) at least one zone (17) for separating and purifying the cracked hydrocarbons, said zone being connected to at least one of the drawing-off lines (16).

In an aspect of the present invention, the electrical heater apparatus comprises at least one induction heating tube (6), e.g. having an induction coil (15) wound around said tube and connected to at least one of the electrical lines (8).

According to another aspect of the present invention, the electrical heating apparatus is a Joule effect heating apparatus, e.g. a resistance element tube comprising, for example, one or more tubes having their ends connected to at least one transformer which is in turn connected to at least one of the electrical lines (8). The resistance element tube heater device can be constituted in particular by one of those specified above.

In a preferred embodiment, the steam cracking device can also comprise at least one post-combustion chamber (10) placed on at least one of the lines (9) for evacuating the combustion gases from the gas turbine (1) and fed with a fuel feed line, preferably identical to the above-described line (3) for feeding the gas turbine, or branching therefrom. The fuel feed line can have one or more burners (11) at its end situated in the post-combustion chamber (10).

The post-combustion chamber (10) can be directly connected to at least one of the chambers (14) for preheating the mixture for cracking, such that the exhaust gases from the chamber (10) in particular can penetrate directly into at least one of the preheating chambers (14).

The post-combustion chamber (10) can also be indirectly connected to at least one of the preheating chambers (14) by being connected initially directly to at least one chamber (13) for superheating the mixture for cracking as already preheated in the chamber (14). Under

such circumstances, the superheater chamber (13) has at least one of the transport and heat exchange lines (12) coming from one of the preheater chambers (14) passing therethrough, with said superheater chamber (13) preferably being directly connected to said preheater chamber. Thus, the exhaust gases from the post-combustion chamber (10) pass initially through at least one superheater chamber (13) and then through at least one preheater chamber (14) so that the gases can exchange their heat with the mixture for cracking flowing inside at least one of the transport and heat exchange lines (12).

In another preferred embodiment, the steam cracking apparatus comprising at least one separation and purification zone (17) for the hydrocarbons cracked in the tube (6) can include at least one line (19) for drawing off at least one of the cracked hydrocarbons, in particular a light hydrocarbon such as an alkane in the range C_1 to C_4 , and in particular methane. At least one line (5) for recovering the cracked hydrocarbon(s) can run, for example as a branch connection, from the drawing-off line (19) and can be connected to at least one of the lines for feeding fuel to the gas turbine (1) and/or optionally a line for feeding fuel to at least one of the above-described post-combustion chambers (10).

When the electrical heating is induction heating, the alternator or electricity generator (4) can be connected to a frequency and power adapter delivering electricity suitable for induction heating the cracking tube (6) where the steam cracking reaction is performed. It is also possible to use a high frequency alternator, in particular at a frequency of the kind specified above for induction furnace heating.

When the electrical heating is performed by means of a resistance element tube, the alternator or electricity generator (4) can be connected to a low voltage or very low voltage transformer.

The steam cracking device can also comprise a network for recovering low or medium pressure steam (e.g. in the range 5 MPa to 10 MPa) by means of a water feed line passing through at least one of the preheater chambers (14) so as to preheat the water and create steam by heat exchange with the combustion gases passing through said chamber(s). This can also be done by recovering heat energy by heat exchange between the water previously preheated in this way and the cracked hydrocarbons leaving the electrical heater apparatus via the drawing-off line(s) (16). Thereafter the steam can be separated from the water and recovered in a steam line. The steam can then be heated and even superheated by heat exchange between the steam and the combustion gases passing through at least one of the preheater chambers (14) and preferably between the steam and the exhaust gas from at least one of the post-combustion chambers (10) passing through at least one of the superheater chambers (13). Under such circumstances, the steam line passes through at least one of the preheater and/or preferably superheater chambers (14, 13) so as to form steam at low or medium pressure.

By way of illustration, Figure 1 is a diagram of apparatus that can be used to implement the method of the present invention.

The cogenerator system comprises a gas turbine (1) coupled to an alternator (4). The gas turbine is fed by an air or oxidizer supply line (2) and by a line (3) for feeding fuel that is preferably gaseous. The cogenerator alternator (4) delivers electricity via an electrical line (8). The hot combustion gases escape from the gas turbine (1) via an exhaust line (19). The exhaust line feeds a post-combustion chamber (10) having burners (11) themselves fed by a fuel feed line (3) branching from the line (3) feeding the gas turbine (1) with fuel. The hot exhaust gases from the post-combustion chamber (10) pass successively through a superheater chamber (13) and a

preheater chamber (14) for exchanging heat with the mixture of hydrocarbons and steam flowing along a transport and heat exchange line (12) which passes in succession through the preheater and superheater chambers (14 and 13). The transport and heat exchange line (12) feeds a plurality of induction heater tubes (6) connected in parallel, only one of which is shown in Figure 1. The induction heater tube comprises a cracking tube in which the mixture for cracking flows, and an induction coil (15) powered by the electrical line (8) coming from the alternator (4). The induction heater tube can be isolated in an enclosure (7). The mixture of hydrocarbons cracked in the tube (6) leaves the tube via a drawing-off line (16), and after being quenched one or more times (not shown in Figure 1) it is subjected to fractioning, separation, and purification in a zone (17), in particular by being compressed and distilled. This zone serves firstly to isolate olefins such as ethylene and propylene via one or more drawing-off lines (18) and secondly light alkanes, e.g. in the C_1 to C_4 range, and preferably methane, via at least one other drawing-off line (19). This line has a cracked hydrocarbon recovery line (5) running therefrom to feed the gas turbine (1) and/or optionally the post-combustion chamber (10) with fuel via one of the feed lines (3).

The gaseous fuel feeding the gas turbine (1) e.g. via the feed line (3) is preferably at a minimum absolute pressure of 1.5 MPa to 2.0 MPa, e.g. at an absolute pressure lying in the range 1.5 MPa to 5 MPa, and preferably in the range 2 MPa to 4 MPa. The gaseous fuel feeding the post-combustion chamber (10), e.g. via the feed line (3), can be at a pressure which is lower than that of the fuel feeding the gas turbine (1), e.g. it can be at an absolute pressure lying in the range 0.2 MPa to 1.0 MPa, and preferably in the range 0.2 MPa to 0.6 MPa.

CLAIMS

1/ A method of steam cracking hydrocarbons, which method consists in heating a mixture of hydrocarbons and steam to a desired temperature that is high enough to crack the hydrocarbons and transform them into olefins, the method being characterized in that the source of energy needed for heating the mixture is supplied essentially by cogeneration using combustion of a fuel to produce simultaneously both heat energy and mechanical work which is transformed into electricity by an alternator or an electricity generator, and in that the mixture is initially subjected to preheating using the heat energy supplied by the cogeneration, and is subsequently heated to the desired cracking temperature by means of electrical heating using the electricity supplied by the cogeneration.

2/ A method according to claim 1, characterized in that the cogeneration uses a fuel selected from at least one of the cracked hydrocarbons, preferably one or more alkanes in the range C_1 to C_4 .

3/ A method according to claim 1, characterized in that the fuel is a gaseous hydrocarbon fuel, preferably comprising one or more gaseous alkanes.

4/ A method according to any one of claims 1 to 3, characterized in that the mechanical work is produced by a heat engine, a gas engine, or preferably a gas turbine.

5/ A method according to any one of claims 1 to 4, characterized in that the cogeneration produces heat energy in the form of hot combustion gases at a temperature lying in the range 400°C to 570°C , and preferably in the range 470°C to 550°C .

6/ A method according to any one of claims 1 to 5,
characterized in that the cogeneration produces the heat
energy in the form of hot combustion gases, with a
fraction of the oxygen thereof being used as oxidizer for
5 performing post-combustion and increasing the heat energy
used for preheating the mixture to be cracked.

7/ A method according to claim 6, characterized in that
the post-combustion provides exhaust gases having a
10 temperature lying in the range 500°C to 1100°C, and
preferably in the range 550°C to 800°C.

8/ A method according to claim 7, characterized in that
the heat of the exhaust gases is exchanged simultaneously
15 with water or steam in one or more boilers to produce
steam at low or medium pressure.

9/ A method according to any one of claims 1 to 8,
characterized in that electrical heating is performed by
20 induction heating.

10/ A method according to claim 9, characterized in that
induction heating is performed at high frequency (HF).

11/ A method according to any one of claims 1 to 8,
characterized in that the electrical heating is performed
25 by the Joule effect.

12/ A method according to claim 11, characterized in that
30 the Joule effect heating is performed using a resistance
element tube in which the mixture for cracking flows.

13/ A method according to any one of claims 1 to 12,
characterized in that ultrasound waves are applied to the
35 mixture of hydrocarbons and steam during cracking.

1000939 0280

14/ A method according to claim 13, characterized in that an ultrasound wave generator is used that is powered by electricity supplied by the cogeneration.

5 15/ Hydrocarbon steam cracking apparatus comprising:

i) a cogenerator system comprising a gas turbine (1) connected to a line (2) for supplying it with air or oxidizer, to a line (3) for feeding it with fuel, and to at least one exhaust line (9) for exhausting hot combustion gases from the gas turbine (1), the turbine itself being coupled to at least one alternator or electricity generator (4) connected to at least one electrical line (8);

10 ii) at least one preheating chamber (14) for preheating a mixture of hydrocarbons and steam, the chamber being connected to at least one of the lines (9) for evacuating hot combustion gases and having at least one line (12) passing therethrough for transporting said mixture and enabling heat to be exchanged therewith;

20 iii) at least one electrical heater apparatus for heating at least one cracking tube (6) connected to at least one of the transport and heat exchange lines (12) leaving the chamber (14), and at least one drawing-off line (16) for drawing off cracked hydrocarbons, said electrical heater apparatus being connected to at least one of the electrical lines (8); and

25 iv) at least one zone (17) for separating and purifying the cracked hydrocarbons, said zone being connected to at least one of the drawing-off lines (16).

30

16/ Apparatus according to claim 15, characterized in that the electrical heater apparatus comprises at least one induction heater tube.

35 17/ Apparatus according to claim 15, characterized in that the electrical heater apparatus is apparatus for Joule effect heating.

10009939.02200

18/ Apparatus according to claim 17, characterized in that the Joule effect heater apparatus comprises one or more resistance element tubes in which the mixture for cracking flows.

19/ Apparatus according to any one of claims 15 to 18, characterized in that it comprises at least one post-combustion chamber (10) placed on at least one of the lines (9) for evacuating combustion gases from the gas turbine (1) and fed by a fuel feed line.

20/ Apparatus according to any one of claims 15 to 19, characterized in that the zone (17) for separating and purifying the cracked hydrocarbons comprises at least one drawing-off line (19) for drawing off at least one cracked hydrocarbon, and in that said drawing-off line (19) has at least one recovery line (5) running therefrom for recovering at least one cracked hydrocarbon and connected to at least one of the lines (3) for feeding fuel to the gas turbine (1).

21/ Apparatus according to claim 19, characterized in that the cracked hydrocarbon separation and purification zone (17) comprises at least one drawing-off line (19) for drawing off at least one cracked hydrocarbon, and in that said at least one drawing-off line (19) has at least one recovery line (5) running therefrom for recovering at least one cracked hydrocarbon and connected to the line for feeding at least one of the post-combustion chambers (10).

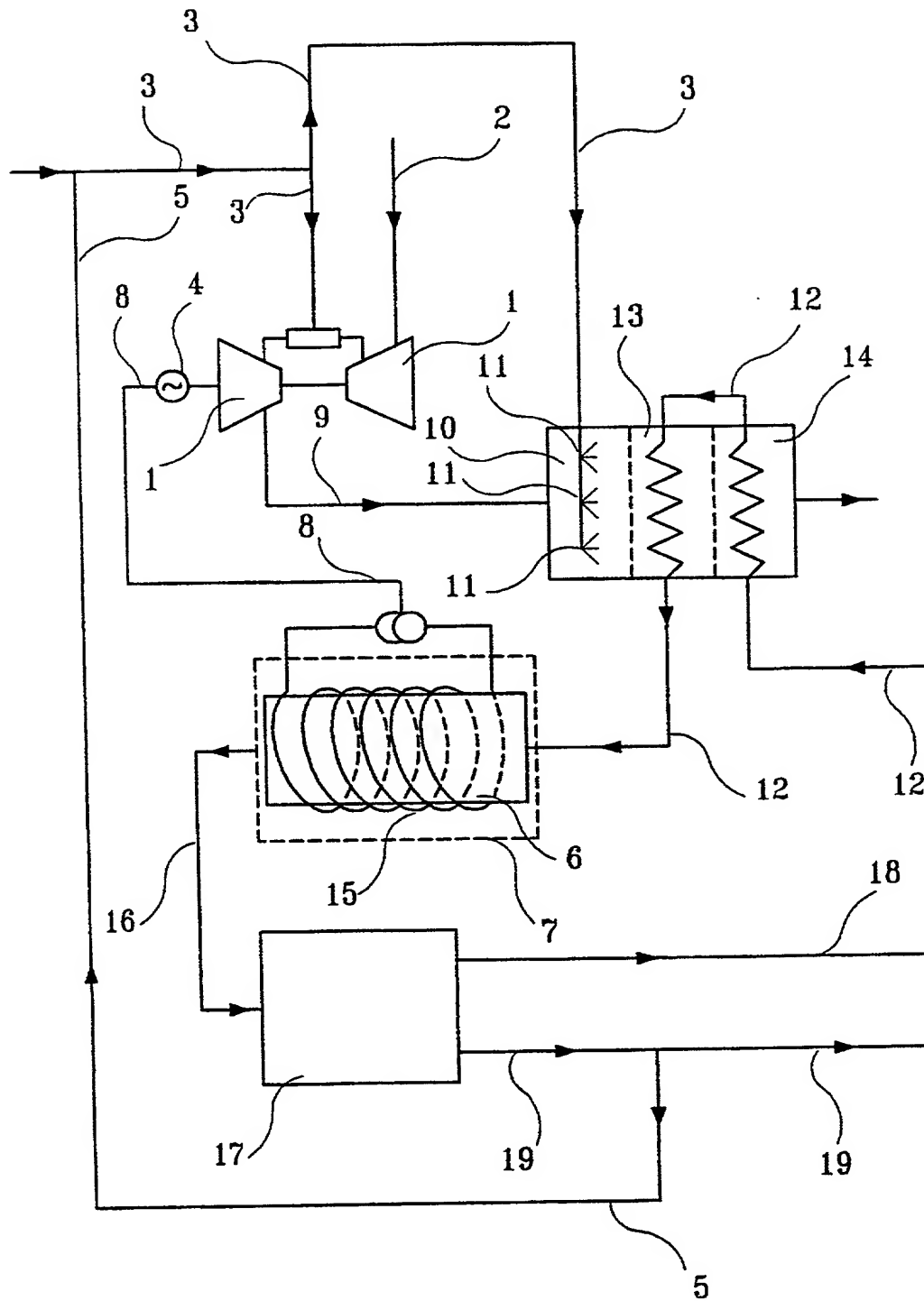


FIGURE 1

Practitioner's Docket No. U 013762-9
PATENT

Optional Customer No. Bar Code

00140

00140

PATENT TRADEMARK OFFICE

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- ☐ original.
☐ design.

NOTE: With the exception of a supplemental oath or declaration submitted in a reissue, a supplemental oath or declaration is not treated as an amendment under 37 CFR 1.312 (Amendments after allowance). M.P.E.P. Section 714.16, 7th Ed.

- ☐ supplemental.

NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.

- ☒ national stage of PCT.

NOTE: If one of the following 3 items apply, then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.

NOTE: See 37 C.F.R. Section 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.

- ☐ divisional.
☐ continuation.

NOTE: Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. Section 1.53(b) (application filing requirements-nonprovisional application).

- ☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: *If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

A METHOD AND APPARATUS FOR STEAM CRACKING HYDROCARBONS

SPECIFICATION IDENTIFICATION

The specification of which:

(complete (a), (b), or (c))

(a) ☐ is attached hereto.

NOTE: *"The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 C.F.R. Section 1.63:*

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____, ☐ as Application No. _____
☐ and was amended on _____ (if applicable).

NOTE: *Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. Section 1.67.*

NOTE: *"The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 C.F.R. Section 1.63:*

(A) application number (consisting of the series code and the serial number, e.g., 08/123,456);

(B) serial number and filing date;

(C) attorney docket number which was on the specification as filed;

(D) title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration;

(E) title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number, e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration.

M.P.E.P. Section 601.01(a), 7th ed.

- (c) ☒ was described and claimed in PCT International Application No. PCT/FR 00/01852 filed on JUNE 30, 2000 and as amended under PCT Article 19 on _____ (if any).

SUPPLEMENTAL DECLARATION (37 C.F.R. Section 1.67(b))

(complete the following where a supplemental declaration is being submitted)

☐ I hereby declare that the subject matter of the

☐ attached amendment

☐ amendment filed on _____.

was part of my/our invention and was invented before the filing date of the original application, above identified, for such invention.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, Section 1.56,

(also check the following items, if desired)

☐ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 C.F.R. Section 1.98.

PRIORITY CLAIM (35 U.S.C. Section 119(a)-(d))

NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by Section 1.63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. Section 119(b) must be filed in the case of an interference (Section 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in Section 1.17(i). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 C.F.R. Section 1.55(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☐ no such applications have been filed.
 (e) ☒ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
 (6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
 AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. SECTION 119(a)-(d)**

| COUNTRY (OR INDICATE IF PCT) | APPLICATION NUMBER | DATE OF FILING DAY, MONTH, YEAR | PRIORITY CLAIMED UNDER 35 USC 119 |
|------------------------------------|--------------------|------------------------------------|---|
| FRANCE | 99/09039 | 7 JULY 1999 | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |

**CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
 (35 U.S.C. Section 119(e))**

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

/ _____
 / _____
 / _____

FILING DATE

**CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)
 UNDER 35 U.S.C. SECTION 120**

- ☐ The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

**ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION**

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. Section 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

JOSEPH H. HANDELMAN, 26179

RICHARD P. BERG, 28145

JOHN RICHARDS, 31053

JULIAN H. COHEN, 20302

RICHARD J. STREIT, 25765

WILLIAM R. EVANS 25858

PETER D. GALLOWAY, 27885

JANET I. CORD, 33778

IAN C. BAILLIE, 24090

CLIFFORD J. MASS, 30086

THOMAS F. PETERSON, 24790

CYNTHIA R. MILLER, 34678

(Check the following item, if applicable)

- ☐ I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.
- ☐ Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

NOTE: "Special care should be taken in continuation or divisional applications to ensure that any change of correspondence address in a prior application is reflected in the continuation or divisional application. For example, where a copy of the oath or declaration from the prior application is submitted for a continuation or divisional application filed under 37 CFR 1.53(b) and the copy of the oath or declaration from the prior application designates an old correspondence address, the Office may not recognize, in the continuation or divisional application, the change of correspondence address made during the prosecution of the prior application. Applicant is required to identify the change of correspondence address in the continuation or divisional application to ensure that communications from the Office are mailed to the current correspondence address. 37 CFR 1.63(d)(4)." Section 601.03, M.P.E.P., 7th Ed

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

Ladas & Parry
26 West 61st Street
New York, N.Y. 10023

(complete the following if applicable)

Since this filing is a [] continuation [] divisional there is attached hereto a Change of Correspondence Address so that there will be no question as to where the PTO should direct all correspondence.

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

20220220 1000939 022802

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other document.

NOTE: Each inventor must be identified by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and by his/her residence, post office address and country of citizenship. 37 C.F.R. Section 1.63(a)(3).

NOTE: Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.63(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997,

Full name of sole or first inventor

Serge BELLET
(Given Name) (Middle Initial or Name) Family (Or Last Name)
Inventor's signature S. Bellet
Date 13 dec 2001 Country of Citizenship FRANCE
Residence CHATEAUNEUF-LES-MARTIGUES, FRANCE FRX
Post Office Address 4, impasse La Fontaine, 13220 CHATEAUNEUF-LES-MARTIGUES, FRANCE

■■■■■■■

Full name of second joint inventor, if any

Jean PINON
(Given Name) (Middle Initial or Name) Family (Or Last Name)
Inventor's signature J. Pinon
Date 17 dec 2001 Country of Citizenship FRANCE
Residence AIX-EN-PROVENCE, FRANCE FRX
Post Office Address Les Pinchinats, Mas Bonnet, 13100 AIX-EN-PROVENCE, FRANCE

■■■■■■■

Full name of third joint inventor, if any

(Given Name) (Middle Initial or Name) Family (Or Last Name)
Inventor's signature _____
Date _____ Country of Citizenship _____
Residence _____
Post Office Address _____

(check proper box(es) for any of the following added page(s)
that form a part of this declaration)

[] **Signature** for fourth and subsequent joint inventors. *Number of pages added* _____

* * *

[] **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____

* * *

[] **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 C.F.R. Section 1.47. *Number of pages added* _____

* * *

[] Added page for **signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 C.F.R. Section 1.47)

* * *

[] Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

[] Number of pages added _____

* * *

[] Authorization of practitioner(s) to accept and follow instructions from representative.

(If no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)

[X] This declaration ends with this page.